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# SURFACE MODIFICATION OF POLY(ETHYLENE TEREPHTHALATE) IN AIR PLASMA

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**Abstract:** This paper reports the modification of a polyester film surface in air plasma at room temperature. In order to evaluate the efficiency of the plasma treatment, the modified surface of the PET films was characterized by contact angle and ATR-FTIR spectroscopy.

***Keywords*:** air plasma; contact angle; PET film; surface.

## Introduction

The functionalization is a common way to introduce new functional groups onto polymeric surfaces in order to obtain new materials.[1] Generally, the functionalization depends on the chemical reactivity of the basic polymer surface. For this purpose, different modification processes are

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possible such as: the introduction of new functional groups, conversion of the functional groups or grafting of some new polymers.[2]

The functionalization can be realized using plasma treatment with non-polymerizable ($N_2$, $O_2$), or polymerizable gases. Plasma polymerization can be induced to any substance which can be converted to gas by reducing the pressure.[3] By using radio frequency discharge, the molecules are energized and they can generate superficial reactive species that can then react with any substance capable of forming a polymer film through the polymerization process. The polymer surface modification occurs by exposure to cold plasma, at a low temperature and a low discharge pressure. Plasma is an ionized gas which contains a large amount of charged atoms, molecules, ions and free radical species. The charging of gas molecules is carried out in a voided chamber in which an intense electric field is created, called RF (Radio Frequency). The emitted electrons are charged with energy which leads to dissociation of the molecules in powerful reactive species. The interaction of the reactive species with solid surfaces results in their chemical and physical modification. The effect of plasma on the material is defined by the reactions occurred between the material and the reactive plasma species[4]. The activation occurs at the polymer surface, where the functional groups are substituted with different atoms from plasma. In this way, the polymer surface is oxidized and the polar, implicitly the hydrophilic character, increases.

The paper reports the successful functionalization of the surface of the Poly(ethylene terephthalate) (PET) film. This polymer has a hydrophobic structure with functional groups at the end of the chains. Under the action of air plasma, some scission of the polymeric chains appears on the surface. Thus, the surface of PET film was modified and the surface structure was analyzed using water contact angle and ATR-FTIR spectroscopy.

## Experimental

PET films, with 30 μm thickness, obtained from TEROM, Romania, were chosen to be treated in plasma. The functionalization took place at 3 and 5 minutes and a power of 60 W. The equipment utilized for treatment was a RF generator with 13.56 MHz. The PET film was cut into 10 × 5 cm samples and washed with ethanol and bidistilled water. The water contact angle was measured with a KSV Instrument, Helsinki, Finland, at room temperature. The spectra of the modified samples were investigated by Attenuated Total Reflectance - Fourier-transform infrared spectroscopy (ATR- FTIR) using a Bruker LUMOS - FT-IR Microscope equipped with ATR reflection module.

## Results and Discussion

The PET films were functionalized by air plasma and, as a consequence, some polar groups were generated on the surface. It is well known that the contact angle values are different due to the changes in surface topography. These changes were observed after 3 and 5 min of plasma treatment.

Table 1 presents the water contact angle values of the modified PET samples.

The obtained values of the contact angle indicate that the sample surface is in the hydrophilic region. The topography of film surfaces undergoes important changes due to the plasma treatment. It is observed that the water contact angle value of untreated PET surfaces was 79.7º and after air plasma treatment it decreases until 40.7º and 15.3º respectively. This phenomenon is due to the fact that after air plasma treatment, some polar groups appear on the surface of the PET film, leading to the decrease of the water contact angle.[5]

**Table 1.** Water contact angle values of treated PET films at 60 W

| Sample treated (min) | Contact angle(º) water |
|---|---|
| 0 min | 79.7 |
| 3 min | 40.7 |
| 5 min | 15.3 |

In order to monitor the evolution of functionalization, the PET samples were characterized by FTIR-ATR spectroscopy. In the ATR-FTIR spectra from Figure 1, increases in intensity of absorptions are observed: stretching vibration located at 1711 $cm^{-1}$ (ν(C=O) attributed to the carbonyl present in the ester group); stretching vibrations of ester groups located at 1237 $cm^{-1}$ (νC(O)-O); stretching vibration of the oxyethylene groups at 1120 $cm^{-1}$ (ν(C-O) sym); vibration attributed to the group ν(O-$CH_2$) and ν(C-C-C) located at 1018 $cm^{-1}$. In the same time, there is an increase of the band at 724 $cm^{-1}$ specific to the vibration of the νC(O)-O (r(C=O) and δ (CCO)) groups attributed to the bending vibration out-of-plane of the aromatic ring. This band provides information about the orientation of the chains in polymer.[6-7]

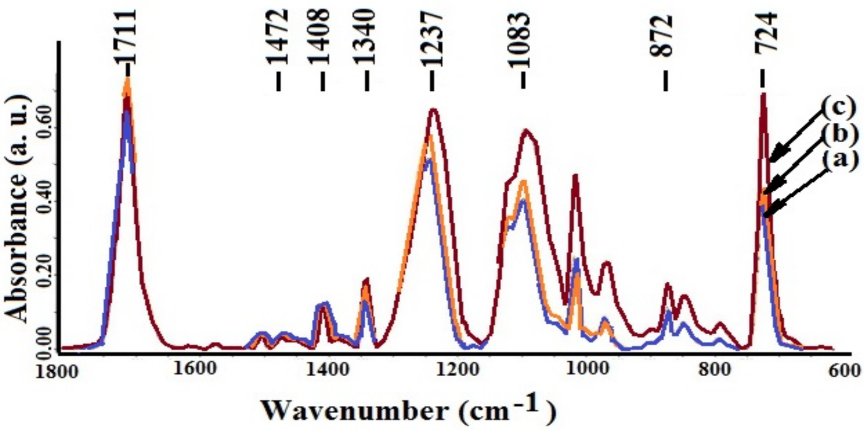


**Figure 1.** ATR-FTIR spectra in 1800 - 600 $cm^{-1}$ region for (a) untreated PET and functionalized in air plasma (b) 3 min and (c) 5 min.

Analyzing the deconvolution bands in the 1800-1650 $cm^{-1}$ range corresponding to the carbonyl stretching vibration of the non-functionalized polyester and after plasma activation for 5 minutes, a series of changes were observed. These modifications occur at the surface of the PET films, especially due to the appearance of free radicals.[8]

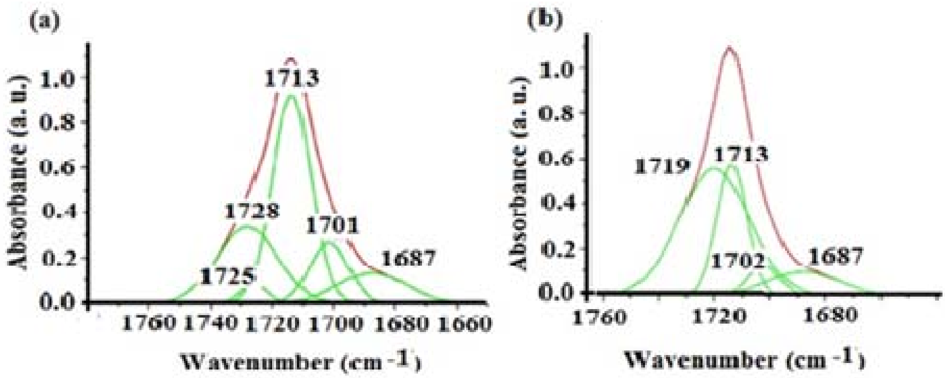


**Figure 2.** Deconvolution of the carbonyl bands of PET film samples (a) untreated and (b) for 5 min treated with air plasma.

In the case of the carbonyl from the untreated film (Figure 2(a)), an ordered structure of the band distribution is observed, with a balance between the distribution of the carbonyl group in the gauche region (represented by the vibration bands located at 1725 and 1728 cm$^{-1}$) and the carbonyl group in the trans region (represented by vibration bands located at 1687, 1701 and 1713 cm$^{-1}$).

The carbonyl group resulted after plasma functionalization for 5 minutes (Figure 2 (b)) has an increased due the increasing the amount of the polar groups.[9] This behavior in intensity determinate an arrangement of the subbands which are moved to higher wavenumber. This band has been assigned to a carbonyl in a less orderly region, respectively gauche.

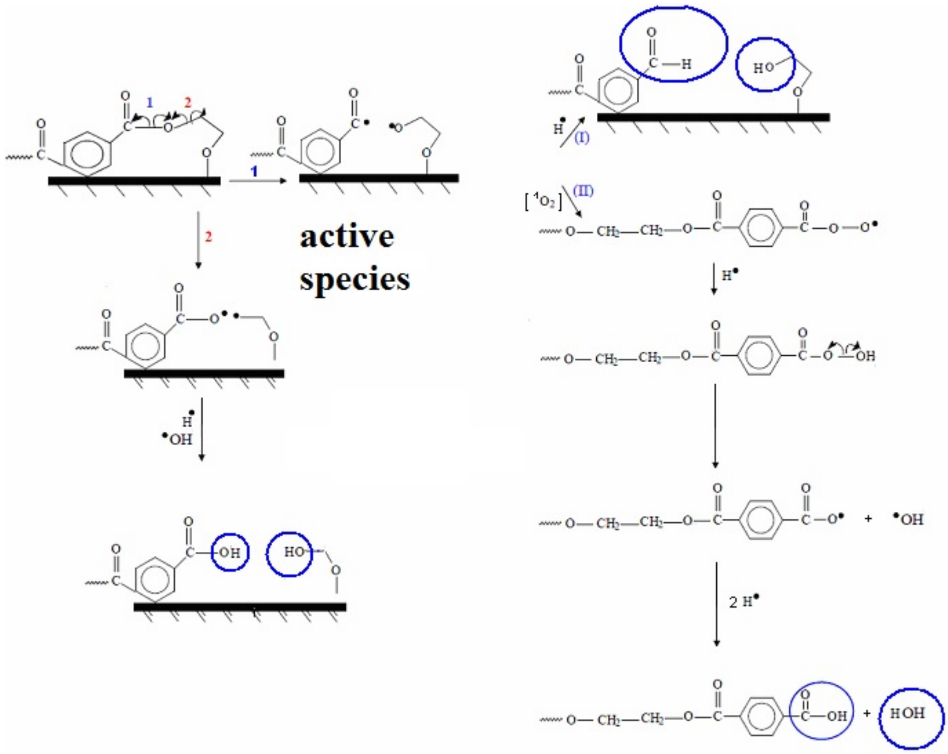


**Figure 3.** Functionalization mechanism of the PET film in air plasma.

In the cold plasma, a relatively weak source is used, and, as a consequence, the polymer substrate is influenced only a few hundred angstroms deep. When the time of treatment is longer, some degradation of the film surface is induced under plasma action and the crystallinity is affected.[10-11] The mechanism of radical generation on the PET surface is a homolitic mechanism, as illustrated in Figure 3. In the first route, the homolitic scindation leads to the formation of the carbonyl and peroxy radicals. Then, in reaction with a hydrogen radical from air plasma atmosphere, aldehyde and hydroxyl groups will be resulted. The reaction with singlet oxygen ($^1O_2$) leads to the formation of the carboxyl groups and water on the PET surface. In the second route, the homolitic scindation leads to the formation of carboxyl and aliphatic radicals, which further lead to the formation of carboxyl and hydroxyl groups on the surfaces. From the ATR-FTIR spectra, structural changes in the surface of the PET film can be observed after plasma treatment, especially increasing the vibrations of the -COO, -CO and –OH groups.

## Conclusions

Our results confirm that under the action of air plasma, the PET surface was activated, leading to an increase of polar groups. These new hydrophilic groups have led to a decrease in water contact angle values. Therefore, the air plasma treatment allows an increase of the surface wettability, achieving materials with high adhesion properties.

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## References

1. Knittel, D.; Schollmeyer, E. Functional group analysis on oxidized surfaces of synthetic textile polymers. *Talanta* **2008**, *76*, 1136–1140.
2. Kostov, K.G.; Nishime, T.M.C.; Castro, A.H.R.; Toth, A.; Hein L.R.O. Surface modification of polymeric materials by cold atmospheric plasma jet. *Appl. Surf. Sci.* **2014**, *314*, 367–375.
3. Keiko, G.; Shohbuke, E.; Kobayashi, Y.; Yamada, H. Wettability control of PET surface by plasma-induced polymer film deposition and plasma/UV oxidation in ambient air. *Colloids Surf. A*. **2018**, *556*, 1–10.
4. Wohlfart, E.; Fernandez-Blazquez, J.P.; Arzt, E.; Campo, A. Nanofibrillar patterns on PET: The influence of plasma parameters in surface morphology *Plasma Process. Polym.* **2011**, *8*, 876–884.
5. Papakonstantinou, D.; Amanatides, E.; Mataras, D.; Ioannidis, V.; Nikolopoulos, P. Improved surface energy analysis for plasma treated PET films. *Plasma Process. Polym.* **2007**, *4*, S1057–S1062.
6. Park, S.C.; Liang, Y.; Lee, H.S; Kim, Y.H. Three-dimensional orientation change during thermally induced structural change of oriented poly(trimethylene terephthalate) films using polarized FTIR–ATR spectroscopy. *Polymer* **2004**, *45*, 8981–8988.
7. Jucius, D.; Kopustinskas, V.; Grigaliunas, V.; Guobiene, A.; Lazauskas, A.; Andrulevicius, M. Highly hydrophilic poly(ethylene terephthalate) films prepared by combined hot embossing and plasma treatment techniques. *Appl. Surf. Sci.* **2015**, *349*, 200–210.
8. Aflori, M.; Drobota M. Combined treatments for the improving of the PET surfaces hydrophilicity. *Dig J Nanomater Bios.* **2015**, *10*, 587–593.

**9.** Aflori, M.; Drobota, M.; Dimitriu, D.Gh.; Stoica, I.; Simionescu, B.; Harabagiu, V. Collagen immobilization on polyethylene terephthalate surface after helium plasma treatment. *Mater. Sci. Eng. B* **2013**, *178*, 1303–1310.

**10.** Aflori, M.; Drobota, M.; Ţimpu, D.; Barboiu, V. Studies of amine treatments influence on poly(ethylene terephthalate) films. *Optoelectron. Adv. Mat.* **2008**, *2*, 291–295.

**11.** Topala, I.; Dumitrascu, N.; Popa, G.; Durand, J. A comparative study of plasma effects on the PET surfaces. *Rev. Chim.* **2008**, *59*, 1263–1265.